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April 1992

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Project: 30.40.01
Analytical Methodology

MINERAL SCIENCES LABORATORIES
DIVISION REPORT MSL 92-38 (IR)

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18 pp

92-04585/

INSTALLATION AND OPERATION OF A SIMULTANEOUS TG/DTA THERMAL ANALYSIS EQUIPMENT

by

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ABSTRACT

A simultaneous thermogravimetry (TG)/differential thermal analysis (DTA) equipment has been acquired by the Mineral Sciences Laboratories for thermal measurements from ambient to 1500°C. The state-of-the-art equipment was assembled, tested and calibrated using standard thermal analysis reference materials and high purity compounds. The different features of the measuring unit, data acquisition, analysis and display were examined for making maximum use of the equipment capabilities.

KEYWORDS

THERMAL ANALYSIS - SIMULTANEOUS TG/DTA - HIGH-TEMPERATURE MEASUREMENTS - STANDARD REFERENCE MATERIALS.

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GENERAL

According to the International Confederation for Thermal analysis (ICTA), thermal analysis is a group of techniques in which some physical property of a substance, and/or its reaction product(s), is measured as a function of temperature while the substance is subjected to a controlled temperature program. Some of the most used thermal analysis techniques today are thermogravimetry (TG), derivative thermogravimetry (DTG), differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermomechanical analysis (TMA), dynamic mechanical analysis (DMA), evolved gas detection (EGD), dielectric constant and emanation thermal analysis (ETA).

Examples of various physical properties measured by thermal techniques are summarized in Table 1.

Table 1: Thermal Properties Measured by Thermal Techniques [1]

Physical property	Derived technique(s)
Mass	Thermogravimetry
	Isobaric mass change determination
	Evolved gas detection
	Evolved gas analysis
	Emanation thermal analysis
	Thermoparticulate analysis
Temperature	Heating-curve determination
	Differential thermal analysis
Enthalpy	Differential scanning calorimetry
Dimensions	Thermodilatometry
Mechanical characteristics	Thermomechanical analysis
	Dynamic thermomechanometry
Acoustic characteristics	Thermosonimetry
	Thermoacoustimetry
Optical characteristics	Thermoptometry
Electrical characteristics	Thermoelectrometry
Magnetic characteristics	Thermomagnetometry

The thermal analysis laboratory of the Mineral Sciences Laboratories operates the most advanced thermal analysis equipment available on the market, enabling it to make significant contributions in internal and external projects at CANMET. The following are the major techniques used in the thermal analysis laboratory of MSL:

- Thermogravimetry (TG)
- Differential thermogravimetry (DTG)
- Differential thermal analysis (DTA)
- Differential scanning calorimetry (DSC)
- Fourier transform infrared spectroscopy (FTIR)
- Gas analysis (GC)

In addition, a state-of-the-art equipment for high temperature simultaneous TG/DTA (Seiko Instrumets) has recently been acquired by the laboratory. High temperature simultaneous TG/DTA is a very valuable technique in the study of the thermal behaviour of minerals, refractory materials, ceramics, metals, alloys, etc. In this technique, changes in the mass and in the thermal characteristics of a substance can be determined simultaneously while the substance is being heated at a selected heating rate and in a selected gaseous environment. In other words, two different physical properties of a substance can be measured simultaneously using only one sample.

INSTALLATION

The newly acquired equipment is a Seiko TG/DTA320 thermal analysis unit with a multitasking station, 5200H. The measuring unit has a temperature range from ambient to 1500^{o}C with a horizontal differential balance mechanism. This high temperature range allows for applications in minerals, ceramics and refrac-

tory materials as well as high temperature metals. A simplified diagram of the equipment is shown in **Figure 1** [2]. The measuring unit was assembled, installed, balanced and interfaced with the multitasking data station which is equipped with a 32-bit 68030 motorola chip and 45M hard disk. A ternary switch was interfaced with the system to allow the use of an existing HP plotter which is also used with two other units in the laboratory. In addition to the swith, a serial to parallel converter had to be installed between the data station and the plotter and changes in the internal wiring of the converter had to be made.

After the installation of the equipment it was found that the high temperature furnace provided was a unifiler type. This type of furnace is not suitable for magnetic materials or materials with magnetic transitions. The surge of current during heating generates an electromagnetic field within the reaction tube causing significant disturbance to the weighing system and often leads to a complete ejection of the sample from the sample container. The furnace was replaced by a byfiler type furnace in which the winding of the Pt-Rh heating element is done in such a way to neutralize the electromagnetic field.

CALIBRATION

1. Sample Temperature

The calibration of sample temperature of the simultaneous TG/DTA unit was carried out by measuring the melting points of various certified reference materials for thermal measurements. The melting point is taken as the onset of the DTA peak. Metal standards were used in the form of wire of 0.25 mm thickness (Johnson Matthey Chemicals Ltd., Puratronic std).

Table 2: Reported Data on the Metal Standards Used

Standard	Purity	m.p., °C certified
Indium	100.00	156.61
Tin	99.999	231.90
Lead	99.999	327.30
Zinc	99.999	419.58
Aluminium	99.999	660.00

Figures 2-4 include TG/DTA diagrams of the various metal standards. The mathematical derivative (DTG) of the TG signal is also shown. The peak onset representing the melting point of each standard was computed and marked on the diagrams. The correlation between the measured and the reported values of the melting points is summarized in the following Table and presented graphically in **Figure 5**.

Table 3: Results of the Melting Point Measurements

Standard	m.p., °C certified	m.p., °C measured (average)
Indium	156.61	156.40
Tin	231.90	231.50
Lead	327.30	324.90
Zinc	419.58	417.00
Aluminium	660.00	660.07

Regression output:

Constant	-1.70636
Std. err. of Y est.	1.414069
R squared	0.999961
No. of observations	5
Degrees of freedom	3
X coefficient(s)	1.00107
Std. err. of coef.	0.003625

The agreement between the measured and reported values was found very good. This is expected in a simultaneous TG/DTA

geometry since both measurements are done on one sample and the temperature is measured by a thermocouple directly attached to the sample holder. The reproducibility of the results was also found high.

2. Sample Mass

The accuracy of the thermobalance was determined by using different NBS standard weights. The thermobalance module is equipped with a weight correction offset for calibration purposes. The correlation between the measured and reported values for the different weights is summarized in the following Table and presented graphically in **Figure 6.**

Table 4: Results of the Mass Calibration

Mass, mg	
Standard	Measured
20	20.059
50	50.278
100	100.114
Regression output:	
Constant	0.134316
Std. err. of Y est.	0.160311
R squared	0.999992
No. of observations	3
Degrees of freedom	1
X coefficient(s)	1.000283
Std. err. of coef.	0.002805

The good agreement between the reported and the measured values for the mass is evident. The reproducibility of the results was found high. The measured values were used, through an available software program, to calibrate the system.

3. DTA Baseline Slope

The determination of the DTA baseline slope consisted of measuring the DTA signal of alumina-filled sample and reference platinum pans under conditions identical to those used during actual sample measurements, **Figure 7**. The DTA signal in the Seiko equipment is presented in microvolts instead of temperature difference. The maximum and minimum observed deviations were 9.1 μV at 480°C and -2.8μV at 1294°C. The baseline can be subtracted from the actual sample DTA signal using the module's software. A DTA baseline slope correction provided with the equipment is used to calculate the offset. Normally, the DTA signal of empty sample and reference pans is determined and the offsets, in μV, are entered in the calibration function at the corresponding temperatures. The offsets are automatically calculated and corrections for the DTA signal are made for each analysis.

4. TG/DTA Analysis of Calcium Oxalate Standard

Calcium oxalate standard reference material was provided by the manufacturer for calibration purposes. Upon heating in and inert atmosphere, calcium oxalate hydrate decomposes at various temperatures with the liberation of H_2O and CO as follows:

$CaC_2O_4.H_2O$	= CaC_2O_4 + H_2O	.... (1)	100-150°C
CaC_2O_4	= $CaCO_3$ + CO	.... (2)	420-520°C
$CaCO_3$	= CaO + CO_2	.... (3)	600-700°C

The three reactions are endothermic. When the heating is carried out in an oxidizing atmosphere, the CO evolving by reaction 2 oxidizes quickly to CO_2 according to the following reaction:

$$CO + \tfrac{1}{2} O_2 = CO_2 \quad .... (4)$$

Reaction 4 is highly exothermic, which renders the total reaction 2+4 exothermic. The TG/DTA diagrams for $CaC_2O_4.H_2O$ heated in helium and in air are presented in **Figures 8 and 9**, respectively.

The effect of the oxidizing atmosphere is clearly demonstrated in the conversion of the middle endothermic DTA peak in **Figure 8** to an exothermic one in **Figure 9**. The results are summarized in Table 5.

Table 5: Results of the Thermal Decomposition of $CaC_2O_4.H_2O$

Reaction	Onset temp., °C		Weight loss, %		
			Theoretical	Observed	
	Inert	Oxidizing*		Inert	Oxidizing*
1	145	145	12.3	12.7	12.8
2(4)	455	461	19.2	18.8	19.0
3	631	642	30.1	30.2	29.9

* Represents reactions 2+4.

These results were quite acceptable and demonstrated the high performance of the simultaneous equipment.

CONCLUSIONS

A newly acquired state-of-the-art thermal analysis equipment for high temperature applications, namely, Seiko TG/DTA320 with a multitasking 5200H station, was installed and tested. Calibration of the thermobalance and the DTA modules was done using standard reference materials. The performance of the equipment was examined and the accuracy and reproducibility of the measurements were found satisfactory. The different features and capabilities of the equipment will be explored and applied to various internal and external projects at MSL.

REFERENCES

1. Wendlandt, W.W., "Thermal analysis", P.J. Elving and J.D. Winefordner, ed., 3rd edition, 1986.

2. Seiko Instruments SSC-5200 Series comprehensive brochure on thermal analysis.

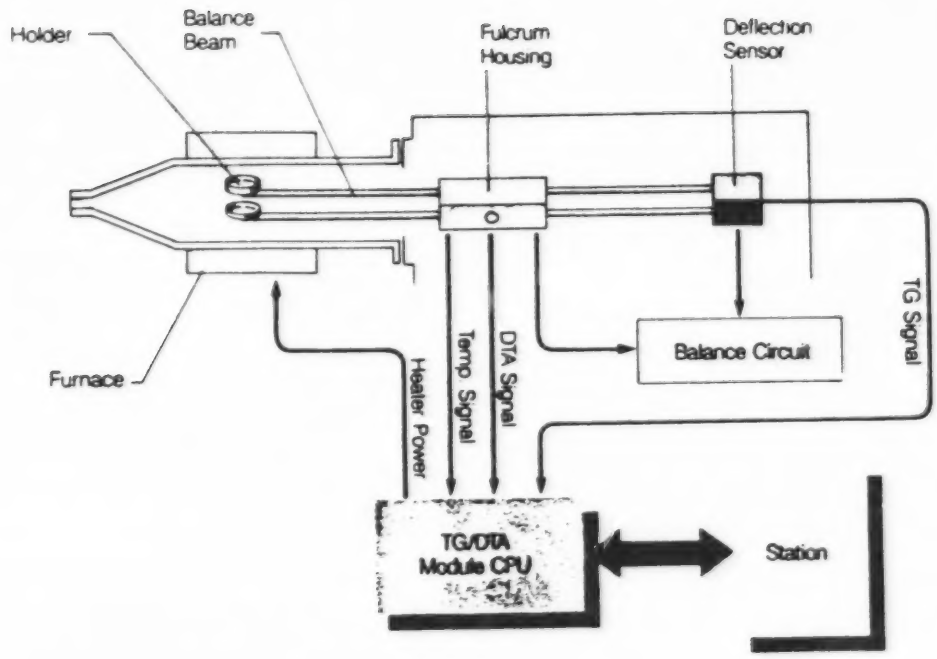

Fig. 1: A simplified diagram for the TG/DTA320 equipment.

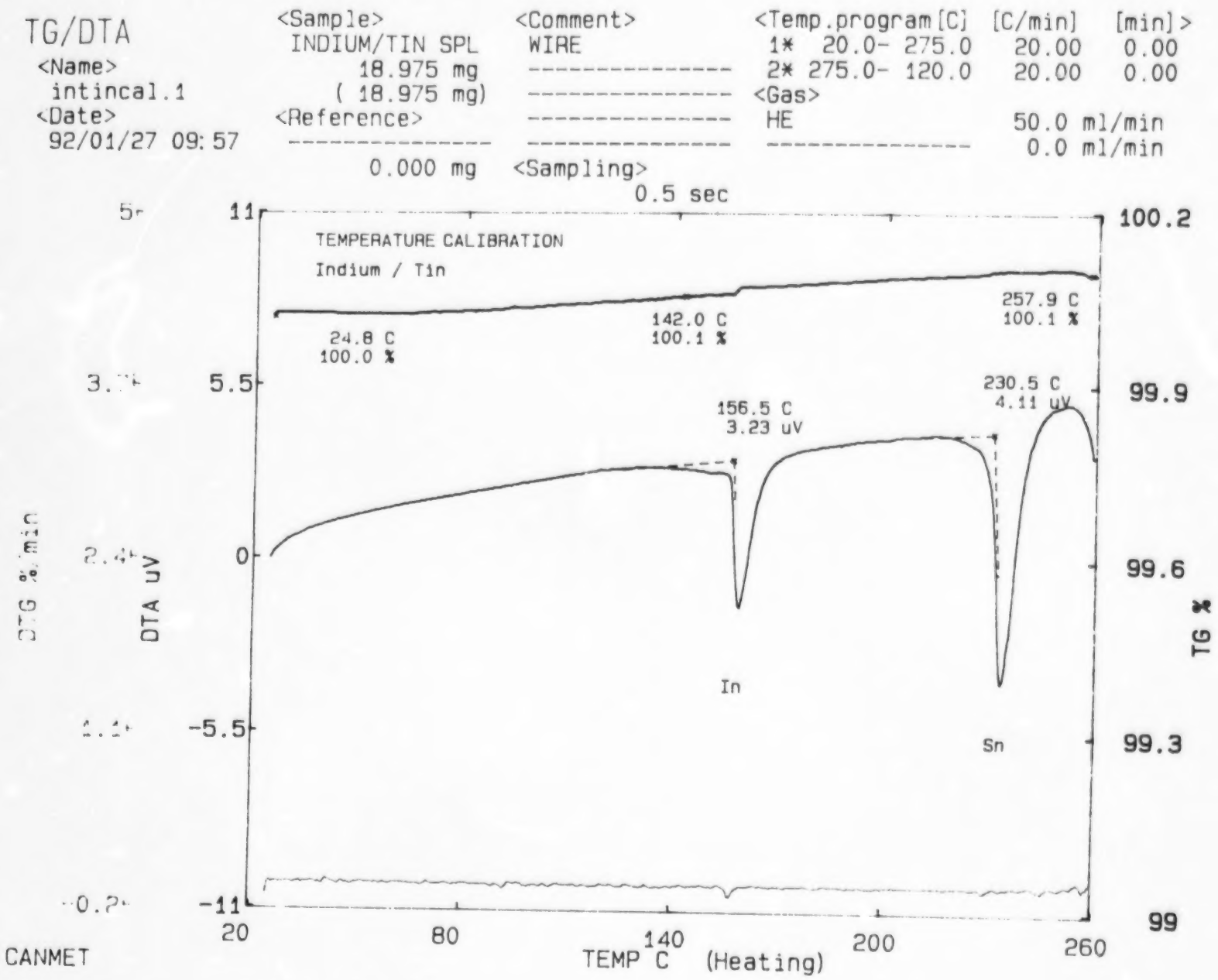

Fig. 2: TG/DTA diagrams of indium and tin standards.

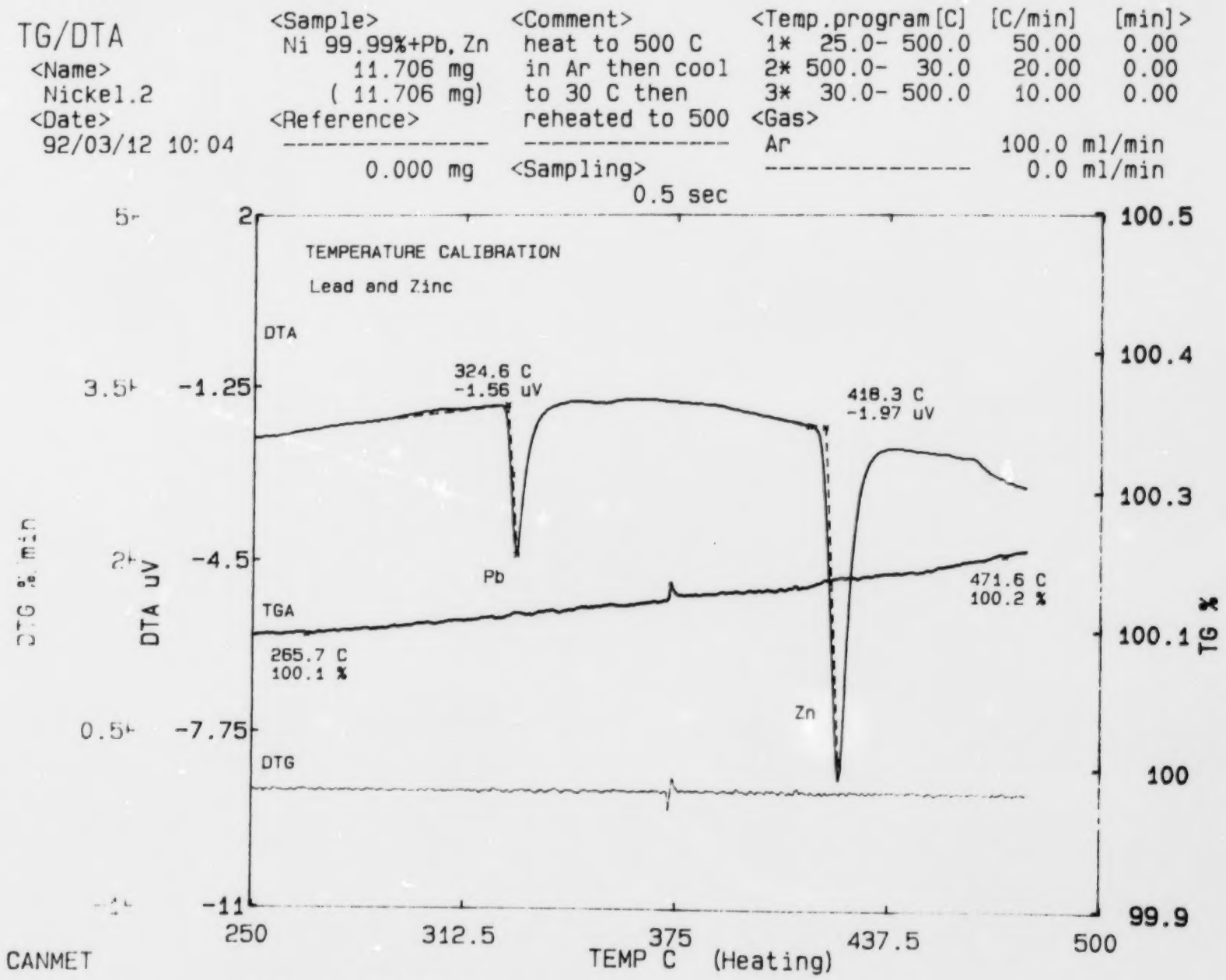

Fig. 3: TG/DTA diagrams of lead and zinc standards.

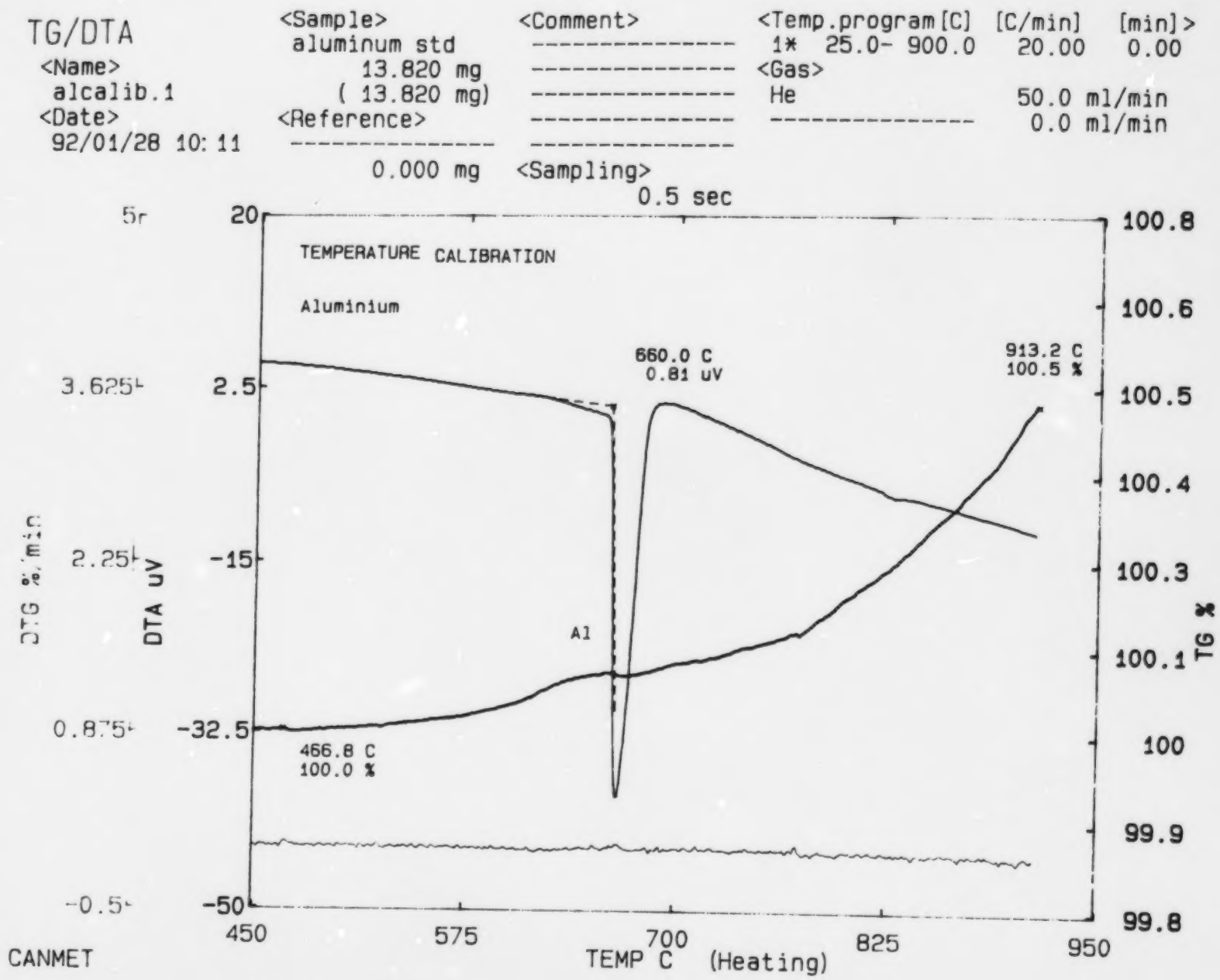

Fig. 4: TG/DTA diagrams of an aluminium standard.

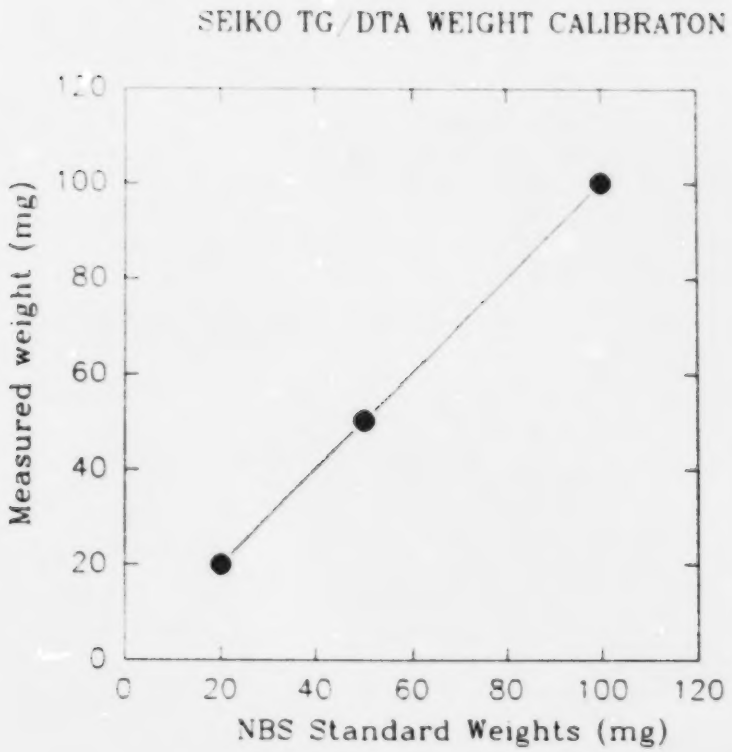

Fig. 5: Correlation between measured and reported melting temperatures.

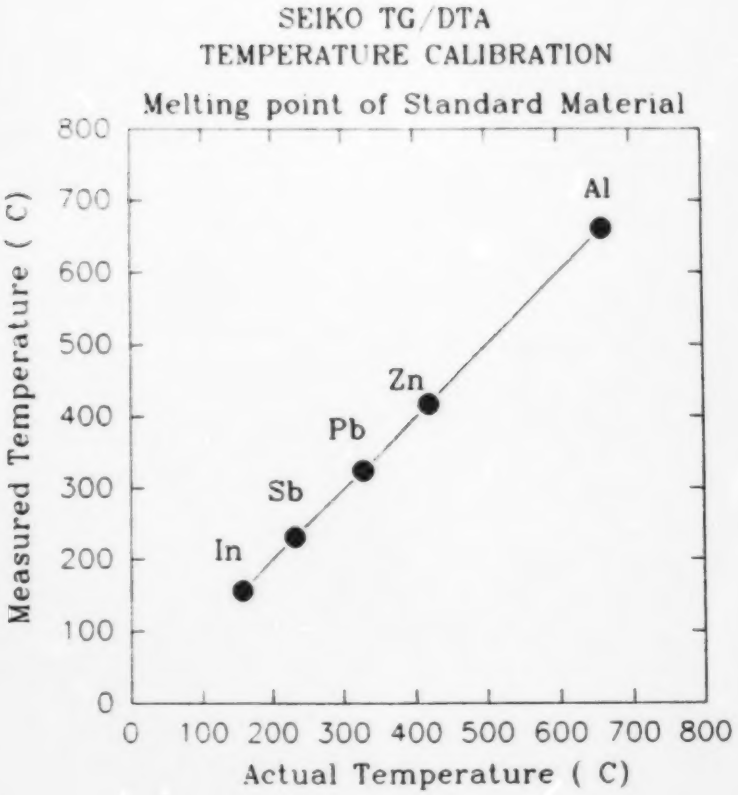

Fig. 6: Correlation between measured and standard weights.

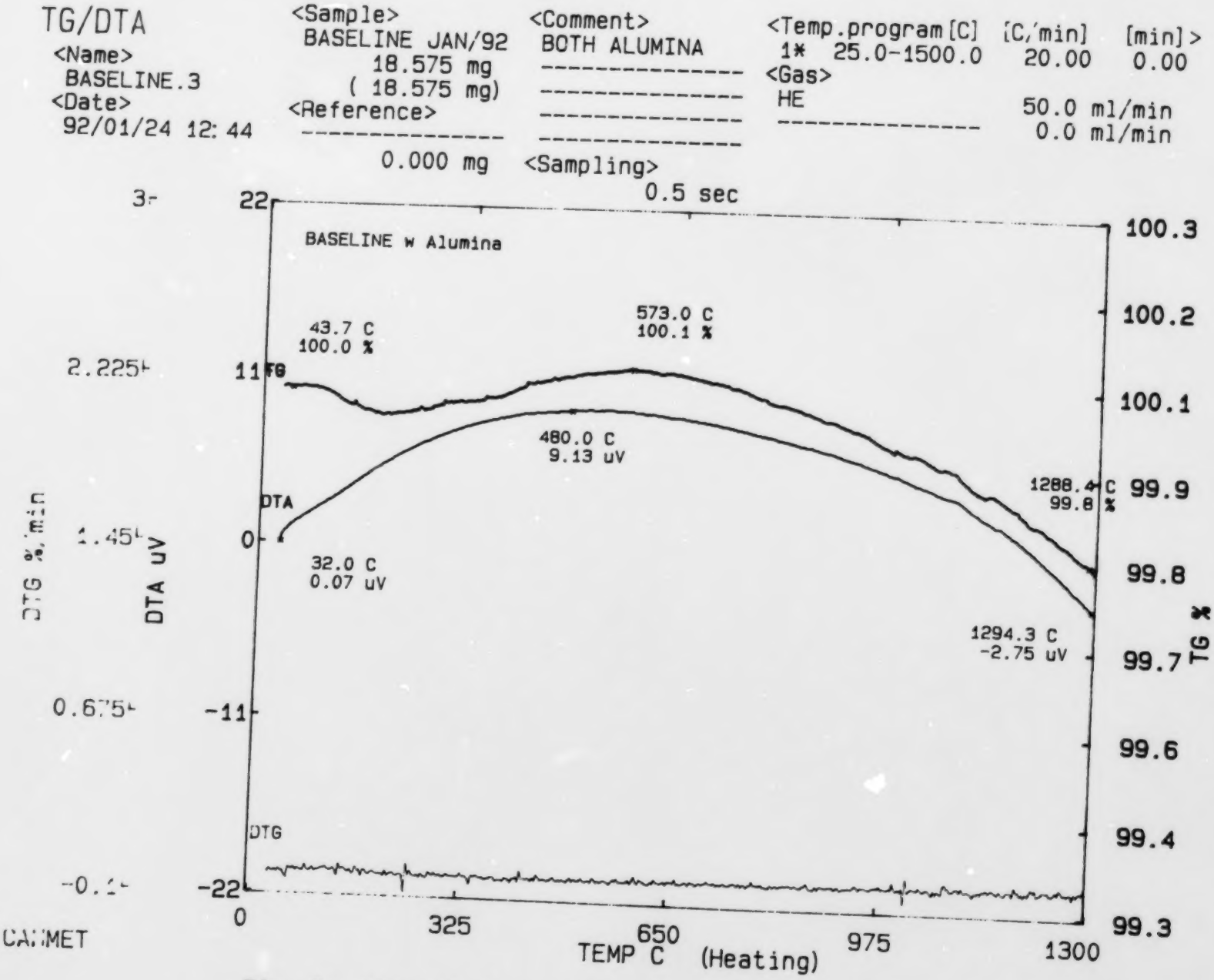

Fig. 7: DTA and TG baselines for the TG/DTA320 equipment.

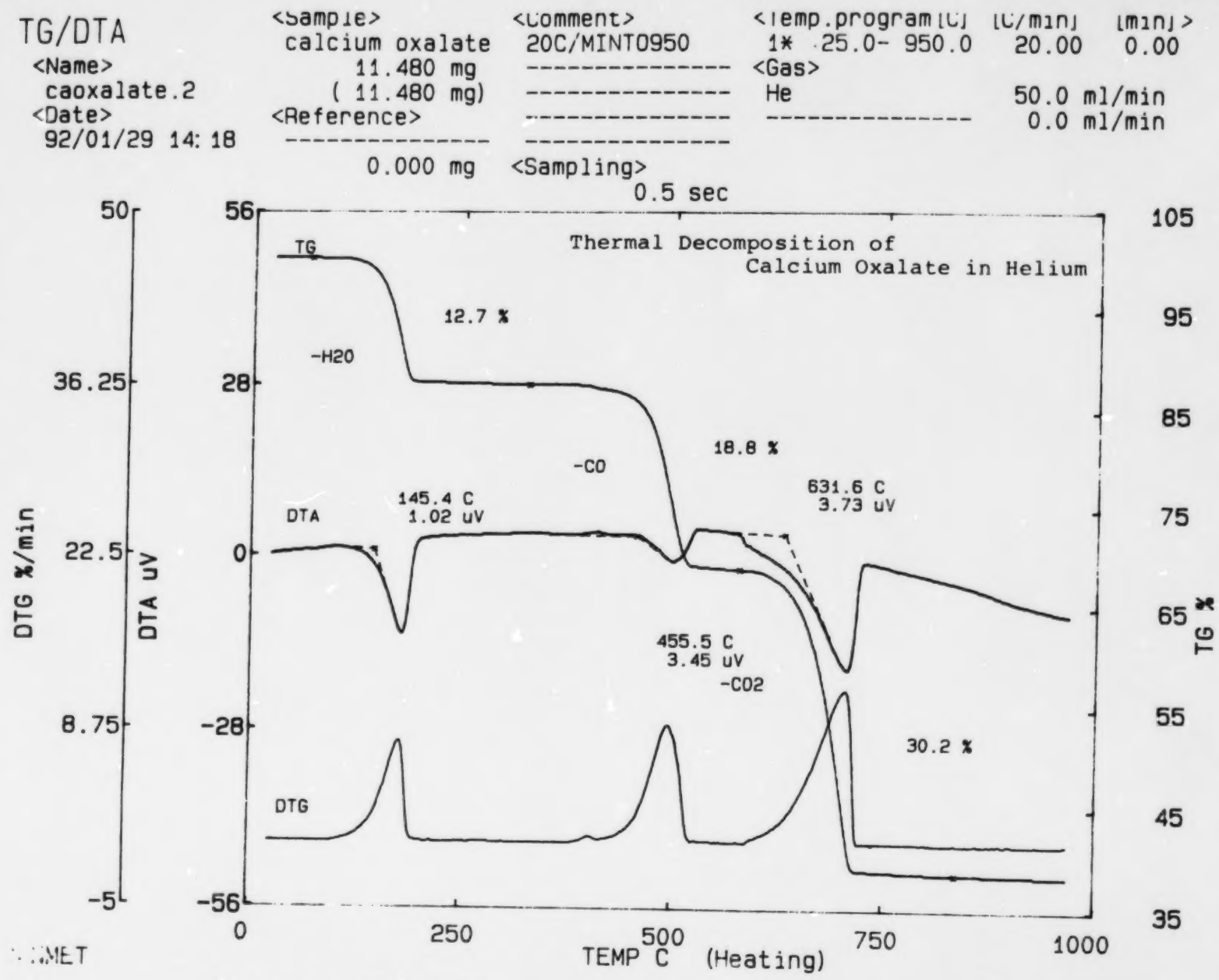

Fig. 8: TG/DTA diagrams of calcium oxalate hydrate in helium.

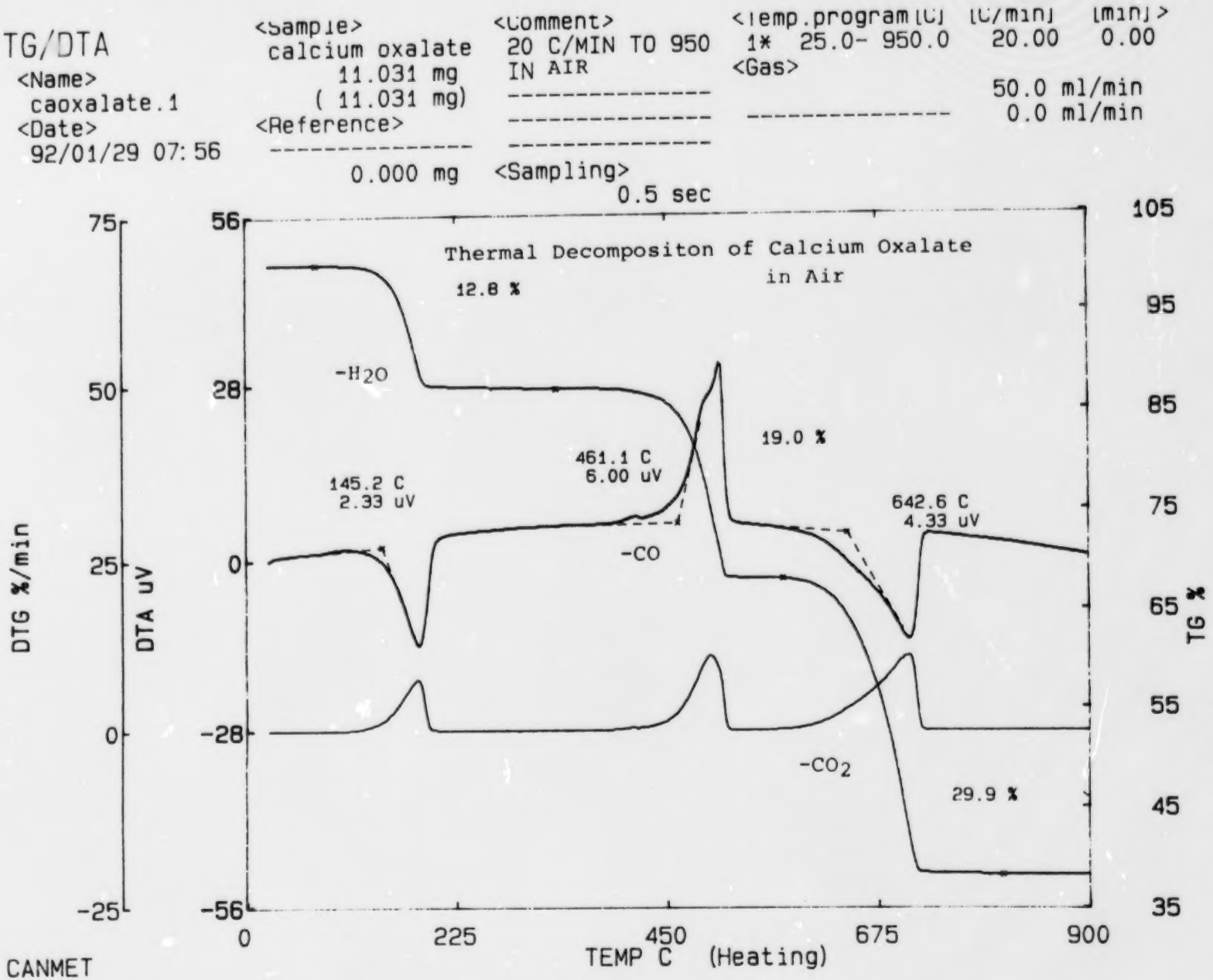

Fig. 9: TG/DTA diagrams of calcium oxalate hydrate in air.